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## Limnological conditions at La Plata reservoir in Puerto Rico: 2008 to 2009<sup>1,2</sup>

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### ABSTRACT

Water column profiles of important limnological indicators (temperature, pH, dissolved oxygen, reduction potential, nutrients) were collected at the center section of La Plata reservoir in north-central Puerto Rico during 2008 and 2009. Temperatures at the surface ranged from values close to 25° C during the hemisphere winter months (December-February) to approximately 30° C during summer (June-August). Total nitrogen and phosphorus concentrations at the epilimnion ( $\leq$  3-m depth) averaged 1.06 mg/L and 50  $\mu$ g/L, respectively. Chlorophyll *a* values averaged 32.4  $\mu$ g/L, which altogether with its nutrient status, would place this reservoir within the eutrophic-hypereutrophic categories. The annual average volume-weighted dissolved oxygen concentration for the reservoir was 3.02 mg/L, a reflection of the delicate ecological condition of this reservoir. The reservoir remains stratified during a large portion of the year ( $\geq$  eight months), inducing prevailing anoxic conditions at the hypolimnion. However, mixing because of incoming flow associated with intense rain events can be common. As a result, the mixing regime of this reservoir is best classified as discontinuous warm polymictic. Runoff associated with intense rainfall is probably the major contributor of hypolimnion dissolved oxygen and nutrient recharge at this reservoir. The distribution of iron (Fe) and manganese (Mn) is strongly

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influenced by the redox status of the system. Solid phases containing these metals exert a dominant role in the cycling of phosphate in the system.

**Key words:** tropical reservoir, eutrophication, water quality, nutrients, anoxia

## RESUMEN

### Condiciones limnológicas en el embalse La Plata en Puerto Rico: 2008 a 2009

Durante los años 2008 y 2009 se obtuvieron perfiles de la columna de agua de importantes indicadores limnológicos (e.g., temperatura, pH, oxígeno disuelto, potencial de reducción, nutrientes) en la sección central del embalse La Plata, localizado en el norte-central de Puerto Rico. Las temperaturas en la superficie oscilaron entre valores cercanos a 25° C durante los meses de nuestro invierno hemisférico (diciembre a febrero) hasta unos 30° C durante el verano (junio a agosto). Las concentraciones promedio de nitrógeno total y fósforo total en el epilimnion ( $\pm 3$  m de profundidad) fueron 1.06 mg/L y 50  $\mu\text{g/L}$ , respectivamente. La concentración promedio de clorofila *a*, 32.4  $\mu\text{g/L}$ , en conjunto con su estado nutricional, colocaría a este embalse dentro de las categorías eutrófico-hipereutrófico. La concentración promedio anual de oxígeno disuelto, ponderado por volumen, para el embalse fue de 3.02 mg/L, lo cual refleja la delicada situación ecológica del mismo. El embalse permanece estratificado durante una gran parte del año ( $\geq$  ocho meses), lo cual induce condiciones prevalecientemente anóxicas en el hipolimnio. Sin embargo, la mezcla de la columna de agua debido al flujo de entrada asociado con eventos de lluvia intensa puede ser común. Como resultado, el régimen de mezcla de este embalse es mejor clasificado como polimíctico cálido discontinuo. La escorrentía asociada con las intensas lluvias es probablemente el mayor contribuyente de oxígeno disuelto y de recarga de nutrientes en el hipolimnio de este embalse. La distribución del hierro (Fe) y manganeso (Mn) está fuertemente influenciada por el estado redox del sistema. Las fases sólidas que contienen estos metales ejercen un papel dominante en el ciclo del fósforo en el sistema.

**Palabras clave:** embalse tropical, eutroficación, calidad de agua, nutrientes, anoxia

## INTRODUCTION

Approximately 70% of the water used for human consumption in Puerto Rico comes from reservoirs (Ortiz-Zayas et al., 2004); thus there is a need to implement protective measures to ensure sustainability of these ecosystems. At present, an analysis of several indicators of ecosystem integrity raises concerns regarding the long-term stability of the reservoir network in Puerto Rico. For example, all major reservoirs are currently listed as impaired for noncompliance with the USEPA aquatic life (dissolved oxygen) criteria (PREQB, 2008). In addition, most reservoirs have lost a significant portion of their storage capacity because of elevated sedimentation rates (Soler-López, 2001), and a significant portion possess near favorable or favorable conditions, from a nutritional standpoint, to sustain a predominant growth of nuisance

algae (Sotomayor et al., 2007; Pantoja et al., 2009). Sixty-three percent of the reservoir population on the island falls in the eutrophic category, and thirty-two percent in the mesotrophic category according to Carlson's (TP)-trophic state index (Martínez et al., 2005).

Tropical lakes and reservoirs are more sensitive than temperate lakes to increases in nutrient supply, exhibiting higher proportional changes in phytoplankton biomass production per nutrient base (Lewis, Jr., 2000). This finding has been attributed to the higher nutrient cycling efficiency of tropical systems, caused by higher metabolic rates as a result of warmer temperatures, coupled with the greater stability of solar radiation characteristic of those latitudes (Lewis, Jr., 1996). The long-term ecological integrity of these systems depends largely upon the establishment of adequate controls of nutrient and organic inputs. A characterization of their basic limnological properties is fundamental for designing sound conservation and management policies that foster their long-term sustainability.

Tilly and García-Saís (1987) evaluated the limnological conditions of La Plata reservoir in Puerto Rico from 1981 to 1982, just seven years after its completion. Close to thirty years later we present a follow-up study aimed at characterizing seasonal and spatial fluctuations of different parameters (e.g., nutrients, dissolved oxygen) that are relevant to the ecological integrity of the system.

## MATERIALS AND METHODS

La Plata reservoir is located between the municipalities of Naranjito and Toa Alta in the north central region of Puerto Rico (Table 1). The reservoir impounds the waters of the Río de La Plata, Río Guadiana, and Río Cañas, and provides close to 35 percent of the total water demand for the metropolitan area of Puerto Rico (Soler-López et al., 2001). The reservoir has a watershed area of 46,879 ha, the largest contributing area of any reservoir in Puerto Rico.

The study was conducted from November 2007 to October 2009. *In situ* depth profiles (one meter resolution) of pH, electrical conductivity, dissolved oxygen, water temperature, turbidity, and oxidation-reduction potential were obtained on a monthly basis at the mid

TABLE 1.—General description of La Plata Reservoir in Puerto Rico. Data from Ortiz-Zayas et al. (2004).

Storage capacity m <sup>3</sup> (10 <sup>6</sup> )	Const. year	Drainage area (km <sup>2</sup> )	Max. depth (m)	Avg. depth (m)	Superficial Area (km <sup>2</sup> )	Renewal frequency times/yr
40.21	1974	468.8	27.0	10.67	3.32	8.2

(18°22'16"N; 66°55'05"W) section of the reservoir. Measurements were taken between the hours of 9:00 to 11:00 with a YSI 6600 multiparameter sonde (YSI Inc., Yellow Spring Instruments, OH) calibrated according to manufacturer instructions the morning of each trip. Data recorded at each depth were the result of measurements collected at 15-s intervals during a three-minute period. Redox potential values

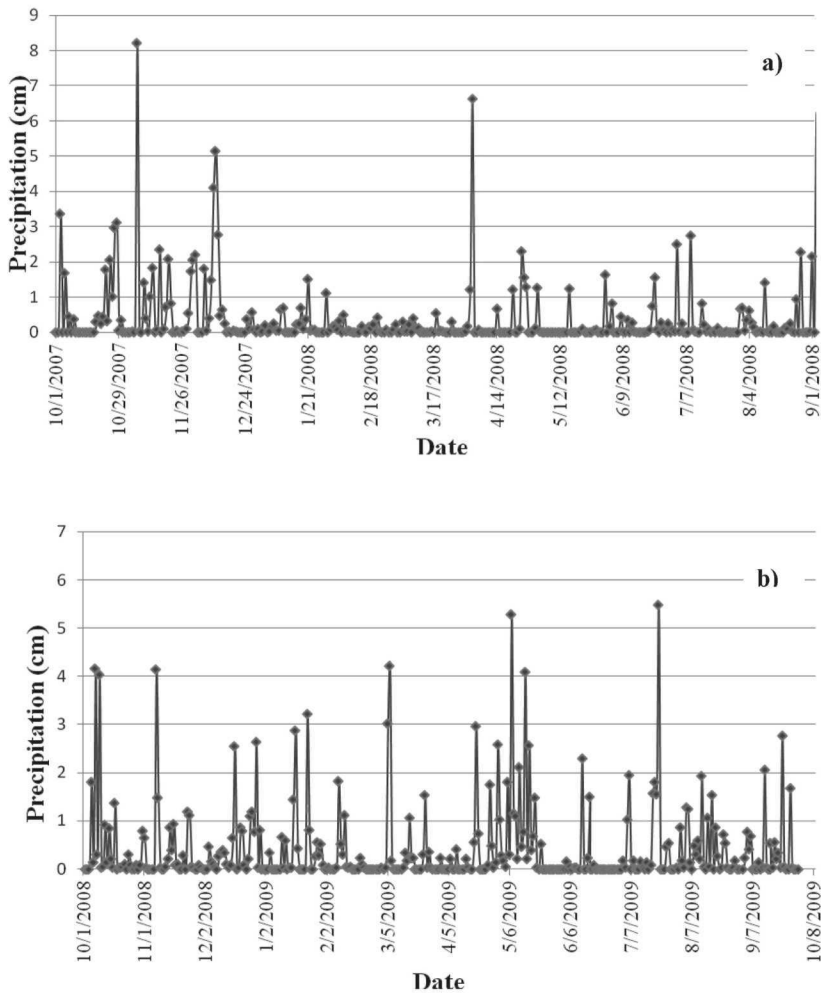


FIGURE 1. Precipitation pattern during the monitoring period: a) 10/07-9/08; b) 10/08-10/09. Figure reconstructed from data collected at USGS station #50045000, located at the dam section of the reservoir. Each point represents a daily cumulative value from data gathered at 15-minute intervals.

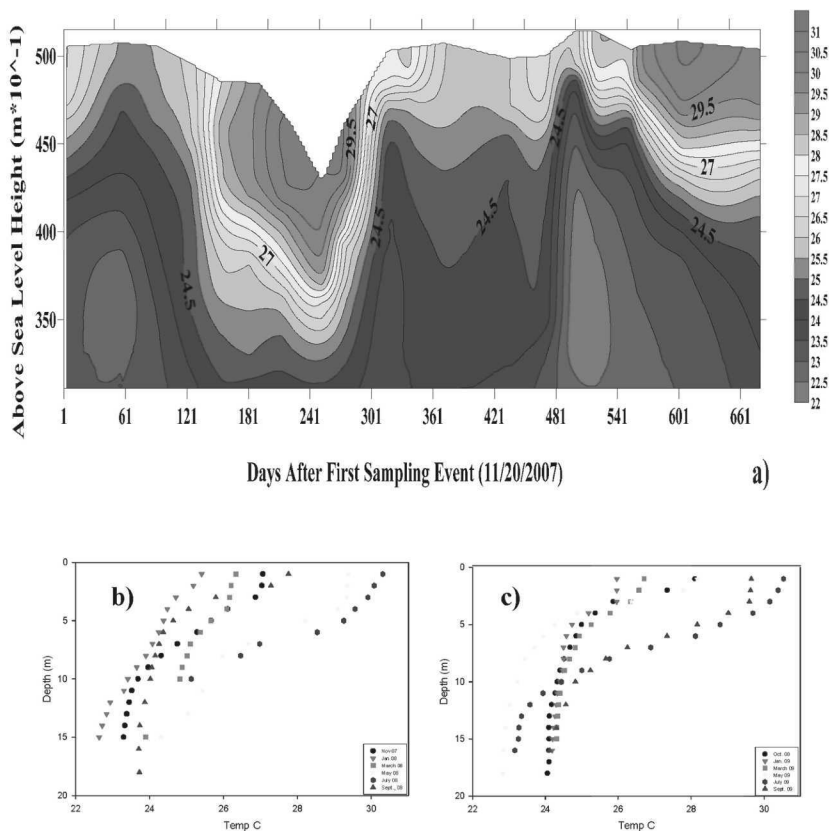


FIGURE 2. a) Depth-time distribution of temperature (°C) isopleths for La Plata reservoir; b) temperature depth profiles for selected months (2007-2008); c) temperature depth profiles for selected months (2008-2009). For full-color figures visit <http://art.eea.uprm.edu/2013-02-07-001.pdf>

( $E_7$ ) are calculated from measurements of oxidation-reduction potentials (ORP) obtained with an Ag/AgCl reference electrode. ORP values obtained with the YSI sonde were converted to SHE (standard hydrogen electrode) values by adding 200 mV. The resulting values were normalized to pH 7 by subtracting 58 mV for every pH unit on the acid side of neutrality or by adding said amount for every pH unit greater than 7. No correction was made for differences in temperature.

Stratification was defined by temperature and/or dissolved oxygen gradients of  $\geq 0.5^\circ \text{C/m}$ ,  $\geq 4 \text{ mg/L/m}$ , respectively. Average epilimnetic, hypolimnetic, and reservoir dissolved oxygen concentrations are volume weighed. Hypolimnetic values were calculated by assuming that the

hypolimnion comprised waters below the average thermocline depth ( $\geq 6$  m). Volume-weighted concentrations were based on one meter resolution strata, with oxygen measurements at the bottom of each stratum. Volume estimates for each layer were based on the most recent bathymetry study conducted by USGS at this reservoir (Soler-López, 2008).

Nutrient status was established from samples collected at 1, 5, 10, 15 and 18 m with a horizontal-type 2-L Van Dorn sampler. Water samples for nutrient analyses were transferred to pre-labeled polypropylene bottles, preserved by acidification ( $\text{H}_2\text{SO}_4$  pH < 2), and transported on ice to the laboratory within three hours after collection. Nutrient analyses included dissolved and total reactive P (EPA method 365.4), total Kjeldhal nitrogen (EPA method 351.2), and nitrate (EPA method 353.2). Samples for nitrate and dissolved phosphorus were filtered through 0.45  $\mu\text{m}$  Gelman acrodisc filters before analysis. Chlorophyll *a* analyses were performed on filtered (on-site) samples (Whatman GF/F) using acetone as the extraction solution (EPA Method 445.0). Analyses were conducted at the Soil and Water Chemistry Laboratory of the Agricultural Experiment Station Center in Río Piedras. Total dissolved Fe, Mn, Al, and Cu were analyzed in separate aliquots by Inductively Coupled Plasma Spectroscopy at the Soil, Plant and Water Laboratory at the University of Georgia, Athens.

## RESULTS AND DISCUSSION

The rainfall pattern at La Plata during Fiscal Year (FY) 2009 (i.e., October 2008 to September 2009) denoted important differences relative to that of FY 2008 (i.e., October 2007 to September 2008). Sixty-two percent of the cumulative rainfall for 2008 fell during the months of September to December, whereas only 35% of the total rainfall fell during the same period for the year 2009 (Figure 1). This factor significantly influenced the limnological properties of this reservoir between years.

### *Temperature profiles*

Temperature profiles at La Plata reservoir are typical of tropical reservoirs and lakes (MacKinnon and Herbert, 1996). Monthly surface temperatures (1 m) ranged from a low value of 24.7° C during January 2008 to values close to 30° C during the hemisphere summer months, June to August (Figure 2). The annual median surface temperature was 26.7° C. A small thermocline ( $< 2.0^\circ \text{C/mn}$  average) was observed throughout the year at a depth between 4 to 6 m (Figures 2b, 2c). Hypolimnion water temperatures varied from 22° C to 27° C with a media value of 24.2° C. Although the overall temperature gradient within the

water column is relatively small ( $< 10^{\circ}\text{C}$ ) compared to that of temperate reservoirs and lakes, at these temperatures (i.e.,  $22^{\circ}\text{C}$  to  $30^{\circ}\text{C}$ ) small temperature fluctuations translate into considerable reductions in the density of water, creating in turn a relatively stable stratified water column (Lewis, Jr., 1996; Townsend, 1999; Sotomayor et al., 2007).

Thermal stratification in tropical reservoirs is particularly sensitive to the effect of winds and runoff from intense rainfall (Lewis, Jr., 2000). Strong winds and storm inflows can promote periodic short-term mixing events during the year that can strongly influence nutrient dynamics and reservoir productivity (Townsend, 1998; Lewis, Jr., 2000). Waters at La Plata reservoir have a relatively short residence time of 45 days (Ortiz-Zayas et al., 2004), thus reflecting frequent displacement by incoming waters. Incoming inflow can have different effects on water column stratification, depending on intensity and duration of the rainfall event and the reservoir level at the time of the event. A moderate rainfall event when the reservoir is relatively full can actually increase the stability of the stratification. The incoming flow is usually denser than impounded water because of its lower temperature and higher suspended sediment content. This condition provokes the incoming waters to intrude below the epilimnion and actually increase stratification stability. On the other hand, a relatively intense storm event can cause holomixis (complete mixing) if isothermal conditions are caused by a large displacement of reservoir waters. The sampling frequency scheme adopted in this study did not allow us to evaluate the frequency of these short-term periodical mixing events. However, the effect of recurrent incoming flows from moderate to intense rainfall on thermal stratification was particularly evident during 2008-2009, a period which did not experience a prolonged dry season.

During the first year (Nov. 2007 to Oct. 2008) thermal stratification was evident in all sampling events (Figure 2). The initial sampling event of November 2008 (11/24/08) was conducted 18 days after a rain event that brought more than three inches of rain within a 24-hour period. The water column was stratified three weeks later even when such an event would have generated enough inflow to favor holomixis. During the hemisphere winter months that followed (Dec. 2007 to Feb. 2008) the temperature gradient within the water column was reduced as a result of superficial heat losses typical of the season. However, even at that point a gradual transition in temperature was observed between the epilimnion and the bottom waters (a clear metalimnion phase could not be distinguished). By March 2008, temperatures in the water column began to increase, with greater changes occurring at the surface. This trend continued until April, by which time surface water temperatures had surpassed the  $28^{\circ}\text{C}$  mark and temperature

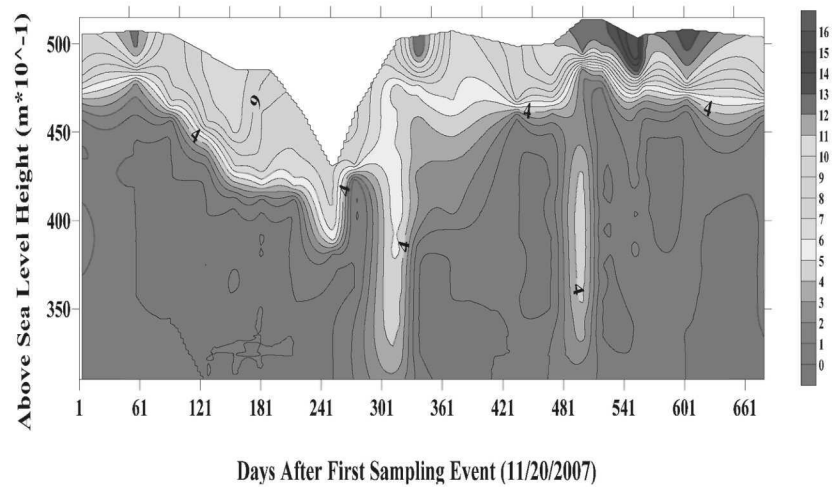


FIGURE 3. Depth-time distribution of dissolved oxygen concentration (mg/L) isopleths for La Plata reservoir.

differences between surface and bottom waters were near maximum levels (Figure 2b).

The end of the 2007-2008 cycle (late August 2008) marked the beginning of a period of frequent moderate to intense rainfall events that

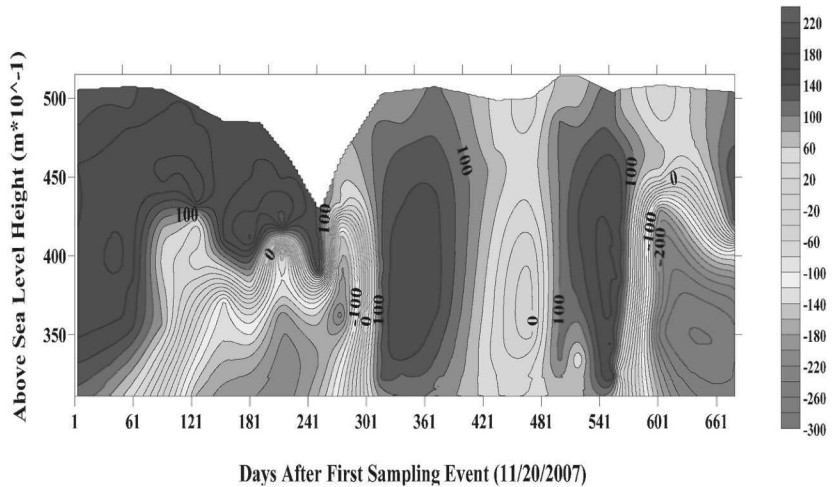


FIGURE 4. Depth-time distribution of reduction potential ( $E_h$ ) isopleths for La Plata reservoir.



continued on throughout the second year. On 30 September 2008 the impact of incoming flow on water column temperature was clearly evident. This finding was the result of various significant precipitation events that occurred during the days prior to our sampling (Figure 1a). Surface water temperatures dropped more than 2° C compared to the temperatures of the previous month (from just over 30° C to 27.7° C) and an even greater difference was observed at the metalimnion. Nine inches of rain were recorded at the dam station in this particular month. This temperature profile pattern persisted until mid November 2008 when the rainfall season ended. At that time the epilimnion waters began to cool down as a result of factors (e.g., evaporative losses of heat and reduced incident solar radiation) associated with our hemispheric winter months.

As stated, during the second year the water column was strongly influenced by the effect of continuous moderate to extreme rainfall events. For example, at the beginning of April (3 April 2009) the water column reflected the effects of an event that brought approximately three inches of rain within a 32-hour period (Figure 2). This amount was followed by more than 9.0 inches of rain during the month of May 2009. As a result, temperatures of the water column were significantly lower than those observed at the same time of the previous year (Figure 2). In fact, the epilimnetic temperatures did not reach the 30° C mark until the month of July, a month later than in the previous year.

In spite of the seasonal and recurring short-term mixing events due to precipitation runoff, Lago La Plata remained thermally stratified during most of the year (early March to early November). Mixing due to a loss in thermal stratification may occur from late November to late February, with the specific dates varying depending on the climatic conditions prevalent in a specific year. Holomixis due to incoming flow associated with intense rain events is common, particularly because of the relatively large watershed/surface area ratio of this reservoir (i.e., 141). As a result, the mixing regime of this reservoir can be classified as discontinuously warm polymictic.

#### *Dissolved Oxygen (and mean Chlorophyll a)*

The annual volume-weighted (column mean) DO concentration for this reservoir was 3.02 mg/L (two-year average), a value slightly higher than that estimated by Tilly and García-Saís in 1982 (i.e., 1.4 mg/L). Said value (3.02 mg/L) accentuates the vulnerability of the long-term ecological integrity of this reservoir. In contrast, the mean epilimnetic volume-weighted DO concentration was relatively high [i.e., 8.85 mg/L, (range: 6.27-12.11 mg/L)]. The latter was expected because of the high productivity of this system. In fact, a positive correlation (Pearson

coefficient = 0.74,  $p = 0.01$ ) was observed between epilimnetic mean volume-weighted DO values and Chl *a* (values not shown). Supersaturation conditions can be common and were particularly prevalent during the second year. The mean Chl *a* concentration was 32.4  $\mu\text{g/L}$ , a concentration which would place this reservoir on the border of the eutrophic-hypereutrophic categories (USEPA, 2009). This Chl *a* concentration value is almost double that reported by Tilly and García-Saís in 1987 (i.e., 16.8  $\mu\text{g/L}$ ). This increase in phytoplankton productivity may not necessarily reflect an increase in nutrient loadings but may respond to a dramatic reduction in the percent coverage by macrophytes, particularly *Eichhornia crassipes* or water hyacinth. Tilly and García-Saís (1987) reported that 40% of the total reservoir surface area was covered by this macrophyte during their study, with 70% of its growth concentrated between their main sampling station (L-1) and the dam. Water hyacinth was practically absent from the specified area (L-1 to dam section) during our study. The disappearance of this physical barrier may have cleared the path to greater light penetration and more favorable conditions for phytoplankton growth.

Dissolved oxygen (DO) profiles from La Plata support our contention that water inflows from moderate to extreme rainfall events largely control the dynamics of this parameter in this reservoir. In addition to bringing cool, denser water into the system, river inflows associated with rainfall events bring oxygenated waters into the hypolimnion. This process is probably the most important mechanism for hypolim-

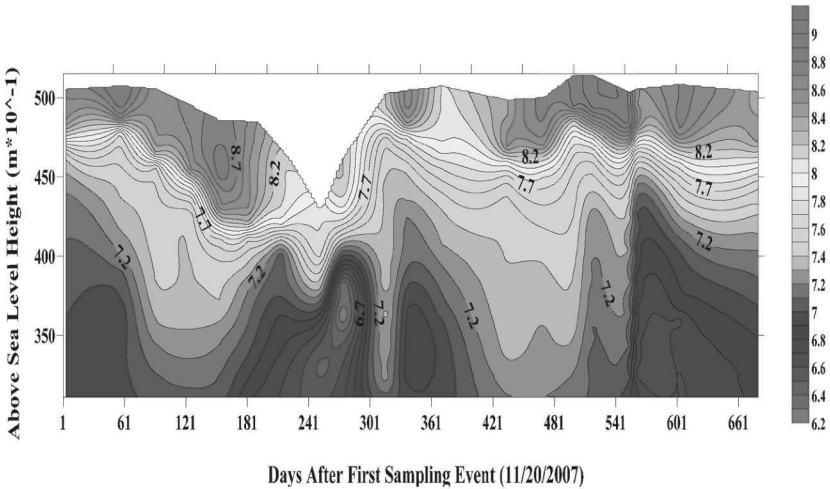


FIGURE 5. Depth-time distribution of pH isopleths for La Plata reservoir.

nion oxygen recharge at this reservoir. A clear example of this effect was evident during September 2008 and April 2009, when a significant increase in DO concentrations was observed below the euphotic layer as a result of several moderate to intense rainfall events that occurred in the weeks prior to our sampling (Figure 3). Hypolimnetic volume-weighted DO concentration reached its highest values on these dates, 3.54 and 4.01 mg/L, respectively. In the absence of precipitation events such as these, the hypolimnion waters remain anoxic during most of the year ( $\geq$  eight months) because of thermal stratification. In fact, volume-weighted concentrations at the hypolimnion did not exceed 2 mg/L during any other period of this study. Hypolimnion waters comprise close to 60% of the total volume, and largely influence the volume weighed mean oxygen concentration for the complete reservoir. The mean hypolimnetic volume-weighted DO concentration during the study period was 0.68 mg/L (range 0 to 4.01 mg/L). The upper quartile ( $Q_{75}$ ) value of hypolimnetic volume weighed concentrations was 0.84 mg/L, indicative of the anoxic conditions that prevail in the bottom waters of this reservoir.

Dissolved oxygen (DO) is essential to the metabolism of all aerobic aquatic organisms. Anoxic conditions cause reduction of fish growth rates, increases in fish mortality, and favor reductive biogeochemical processes such as hydrogen sulfide production and the release of phosphorous (P) and heavy metals (e.g., Fe, Mn) from bottom sediments (Wetzel, 2001; Breitburg, 2002).

#### *Oxidation reduction potential*

The redox potential is a measure of the relative concentrations of oxidized to reduced members in a particular reaction. In general, reductive transformations bring about a considerable degradation in water quality, and intensive treatment is required for transformation into potable use. Reducing conditions (i.e.,  $<150$  mV to negative potentials) bring about the conversion of nitrate ( $\text{NO}_3^-$ ) to ammonia ( $\text{NH}_3$ ), the reduction of iron [ferric ( $\text{Fe}^{3+}$ ) to ferrous ( $\text{Fe}^{2+}$ )], manganese ( $\text{Mn}^{4+}$  to  $\text{Mn}^{2+}$ ), and sulfur [sulphate ( $\text{SO}_4^{2-}$ ) to sulphide ( $\text{S}^{2-}$ )], as well as the production of methane. These transformation reactions have a significant impact on the dynamics of nutrient and contaminant release from bottom sediments into the water column.

As stated previously, tropical lakes and reservoirs are prone to undergo extended periods of hypolimnion anoxia, thus becoming susceptible to developing reducing conditions in their bottom waters. Such a scenario is evident at La Plata reservoir. During the first year, when the effects of frequent intensive rains were minimal, reducing conditions ( $E_r < 300$  mV) at the hypolimnion were prevalent from February

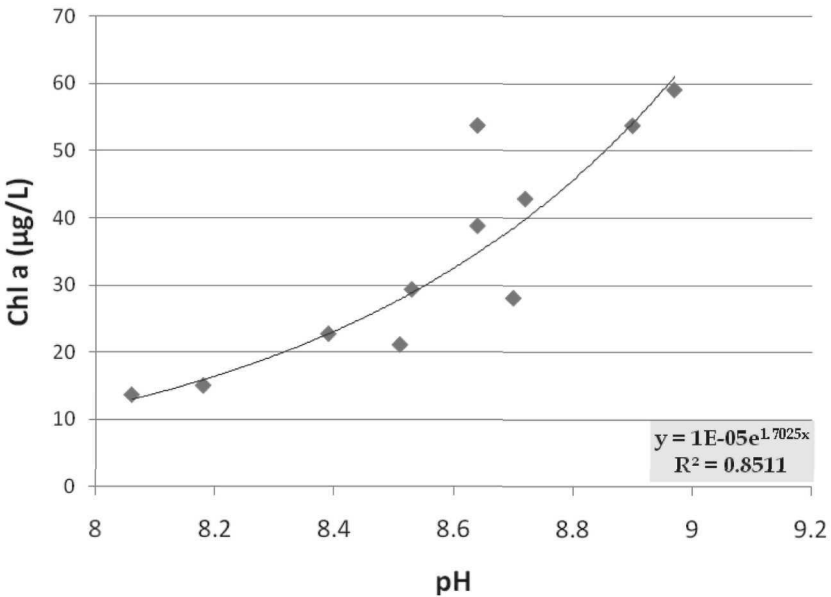


FIGURE 6. Relationship between pH and chlorophyll  $\alpha$  in the surface waters (one meter) of La Plata reservoir.

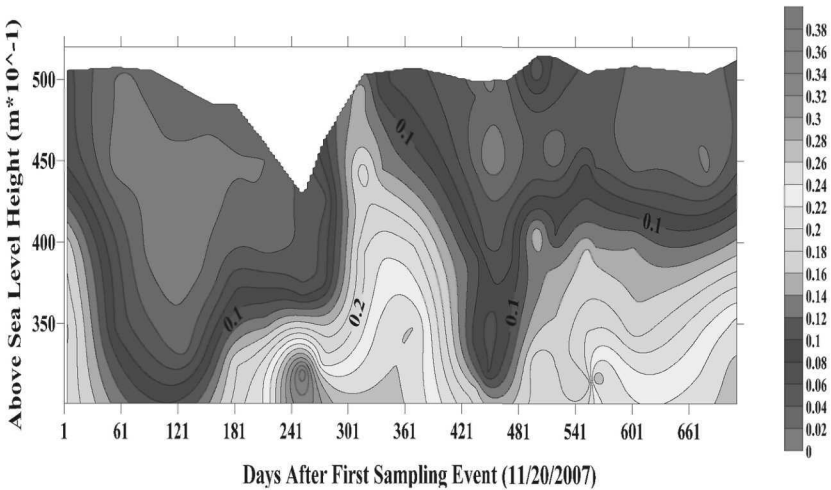


FIGURE 7. Depth-time distribution of total phosphorus (mg/L) isopleths for La Plata reservoir.

2008. By late July 2008, reducing conditions reached to a few meters below the surface (Figure 4). The median  $E_h$  value at the hypolimnion from mid May to late July 2008 was 10.06 mV. The intensive rainfall events of September 2008 ameliorated the situation by bringing oxygenated waters into the system. At this time, median values at the hypolimnion increased to 340 mV. During 2008-2009 said pattern of prolonged reducing conditions at the hypolimnion was disrupted by the rainfall events of April and May 2009. Highly reducing conditions were once again evident during July 2009 (median at hypolimnion of 12.10 mV) and lasted until the start of the rainy season in September 2009.

The deleterious consequences which extended periods of reducing conditions have on water quality require some action to address this issue. Although hypolimnion oxygenation is gaining more popularity as a remediation technique, said alternative may not be as practical at this reservoir. First, as stated, waters at this reservoir have a relatively low retention time. The massive runoff generated from storm events could compromise the physical security of any oxygenation system in-

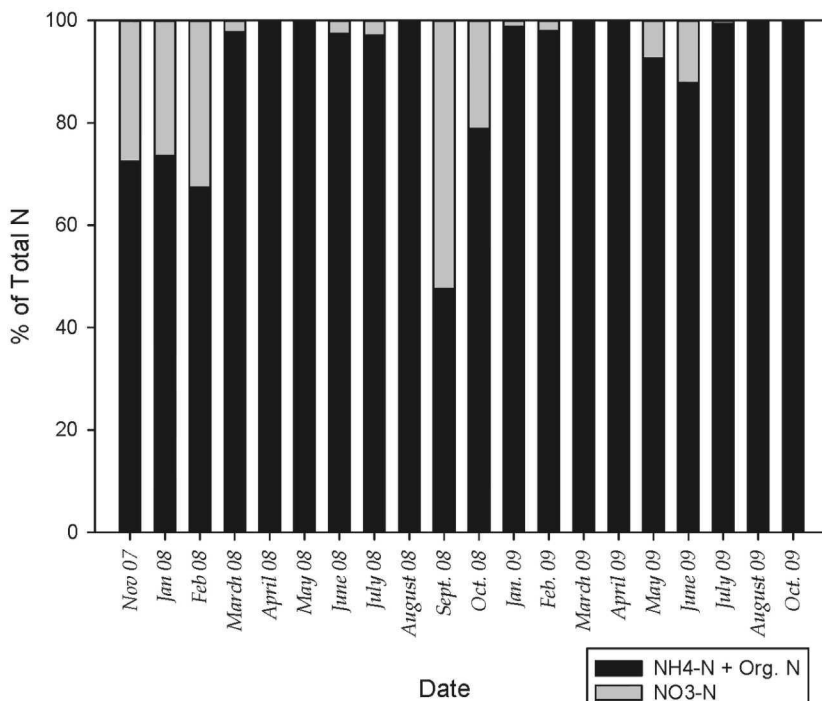


FIGURE 8. Relative composition of total nitrogen at the epilimnion.

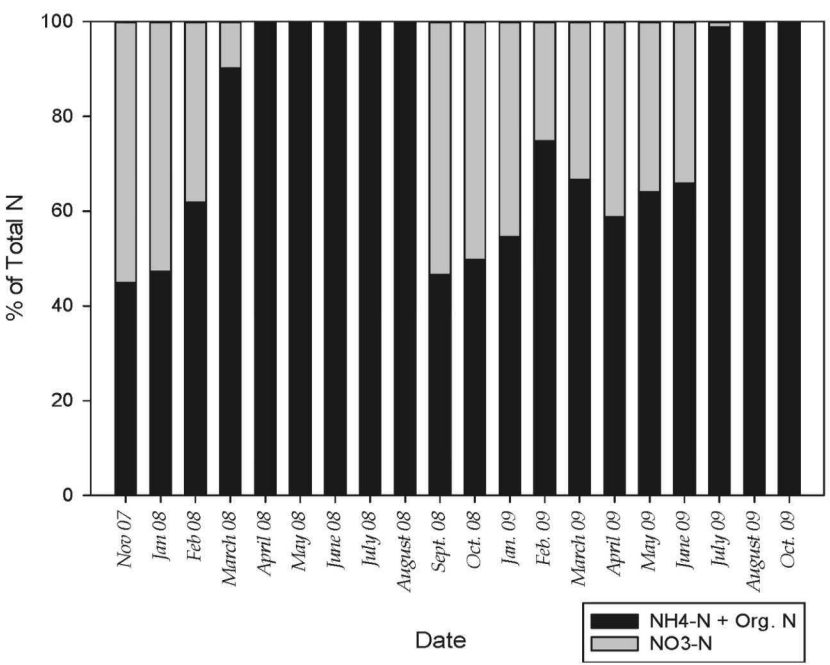


FIGURE 9. Relative composition of total nitrogen at the hypolimnion.

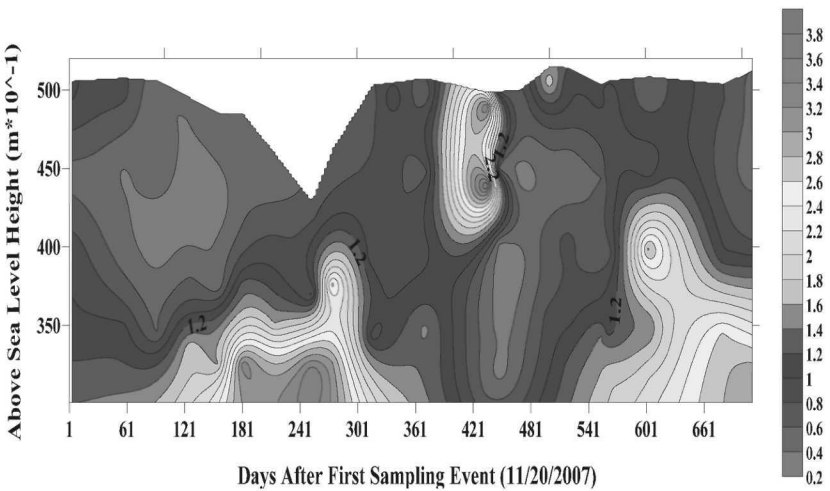


FIGURE 10. Depth-time distribution of total kjeldahl nitrogen (mg/L) isopleths for La Plata reservoir.

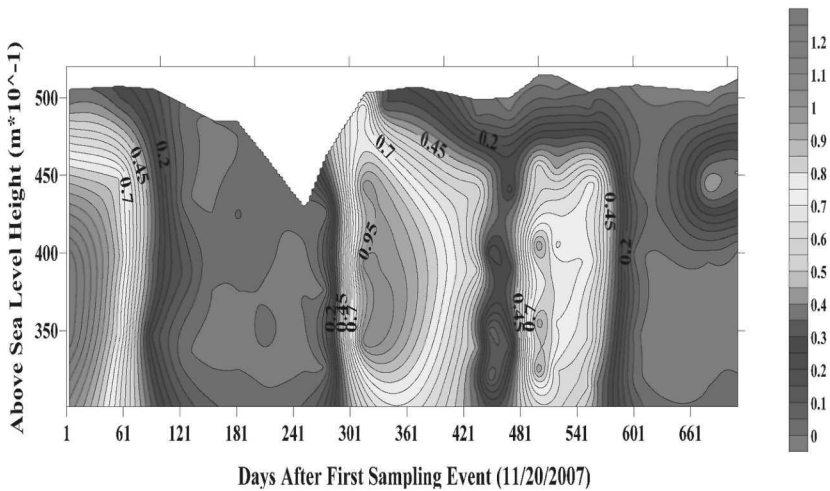


FIGURE 11. Depth-time distribution of  $\text{NO}_3\text{-N}$  (mg/L) isopleths for La Plata reservoir.

stalled. A more sustainable alternative could be the implementation of a watershed management program geared to significantly reduce the organic matter and nutrient loads entering the system. Usually these are long-term strategies that require significant modification in social behavioural patterns. A mid-term compromise could involve a combination of both strategies.

*pH*

The mean epilimnion pH was 8.43 (range 7.52 to 8.97) and was higher than that of the hypolimnion (avg. 7.20; range 6.46 to 7.58) (Figure 5). A positive exponential relation was observed between pH and Chl *a* values at the surface (Figure 6). Increased water pH at the epilimnion is a result of photosynthetic activities (i.e., dissolved carbon dioxide consumption) from the algal community. The biggest hypolimnetic pH drop coincided with periods of highly reducing conditions. Although mineralization rates of organic matter under anoxic conditions are generally thought to be slower than those under oxic conditions, a substantial portion of the total carbon degradation in systems such as that at La Plata could come from anoxic-driven processes. These reactions, which are generally accompanied by a significant drop in pH, could explain the results observed in July-August 08 and June 09.

## Phosphorus

Phosphorus (P) is often identified as a limiting factor for biological productivity in surface waters. Total phosphorus concentration at the

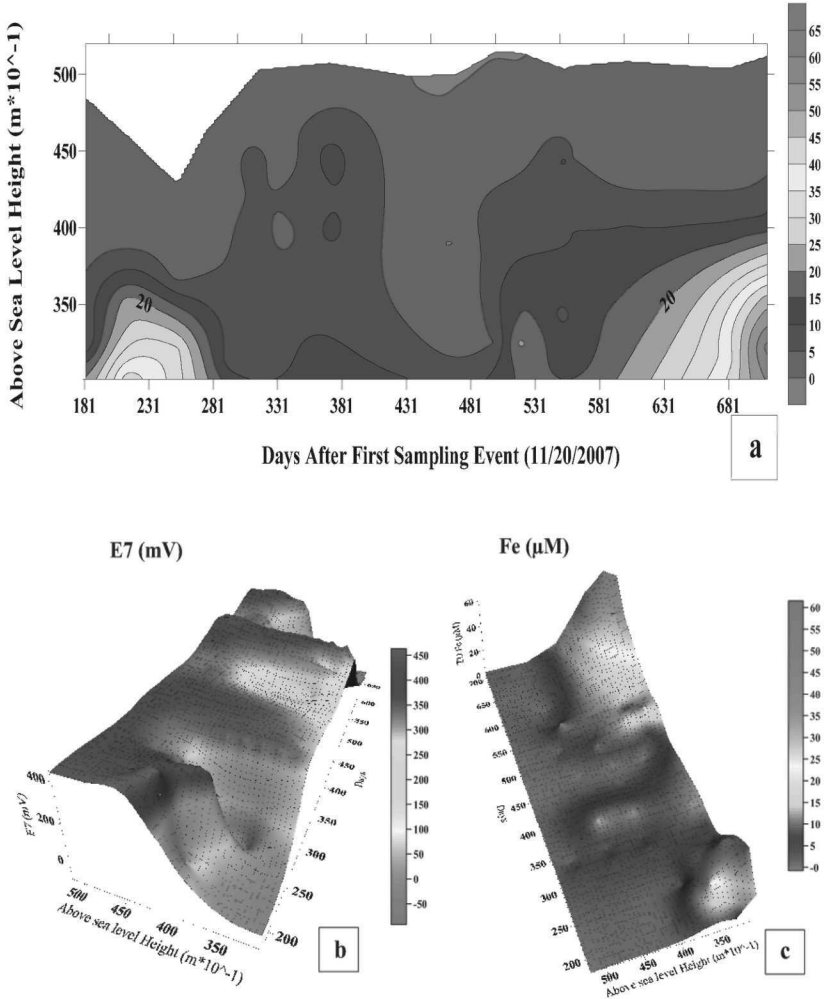


FIGURE 12: a) Depth-time distribution of total dissolved (TD) Fe (μM) isopleths at La Plata reservoir; b) tridimensional plot of variations in reduction potential ( $E_7$ ) with time; and c) tridimensional plot of variations in TDFe with time.

epilimnion averaged 50  $\mu\text{g TP/L}$  (range 12 to 148  $\mu\text{g TP/L}$ ) over the study period (Figure 7). This range falls within the eutrophic category according to Carlson's trophic state index and is much higher than the reference criteria of 23  $\mu\text{g TP/L}$  proposed for reservoirs of Puerto Rico (Martínez et al., 2005). Total P concentrations in the hypolimnion waters were much higher than at the surface, averaging 153  $\mu\text{g TP/L}$



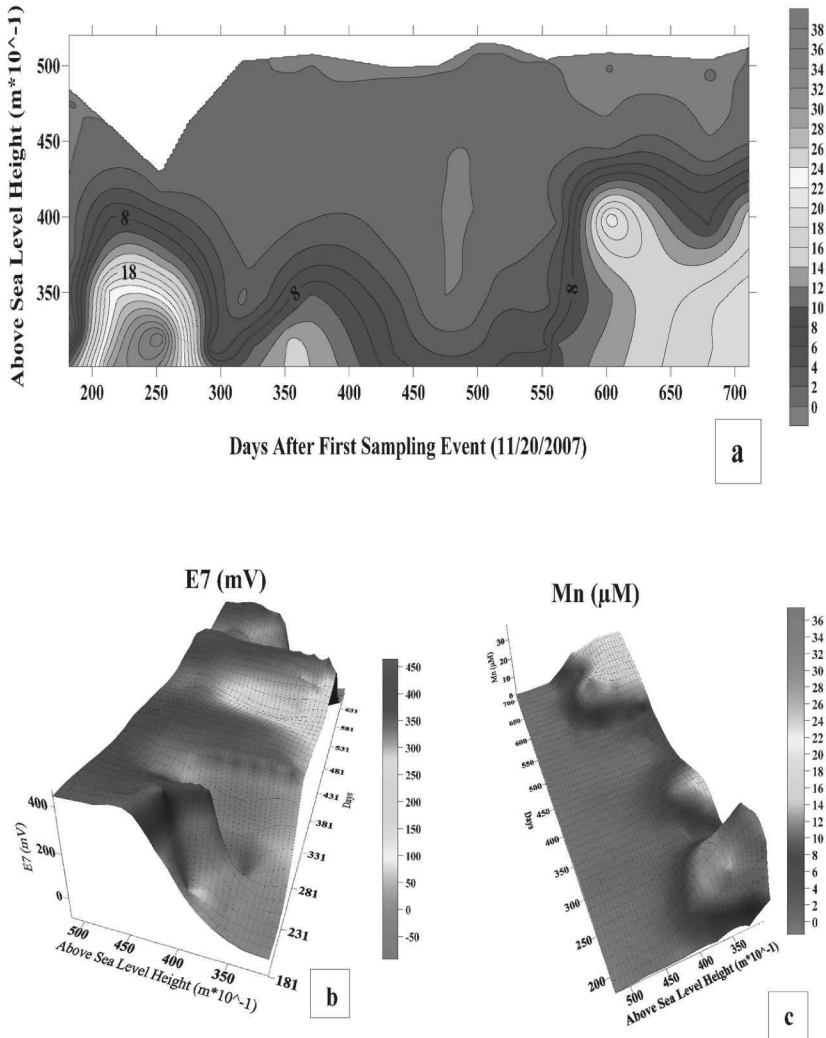


FIGURE 13: a) Depth-time distribution of total dissolved (TD) Mn (μM) isopleths at La Plata reservoir; b) tridimensional plot of variations in reduction potential ( $E_7$ ) with time; and c) tridimensional plot of variations in TDMn with time.

(range 12 μg TP/L to 378 μg TP/L) over the study period. This range of values might support intense algae blooms upon mixing caused either by strong wind or water currents, or by the losses of thermal stratification. The distribution of phosphorus in reservoirs is largely controlled

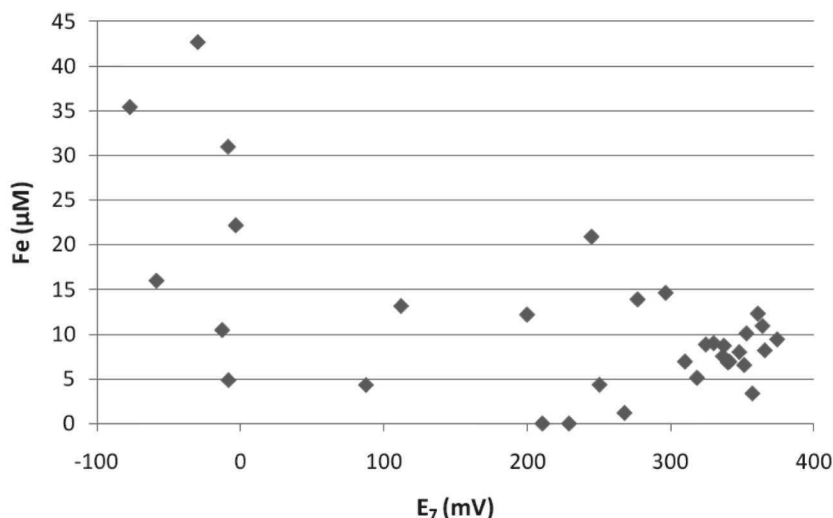


FIGURE 14. Relationship between reduction potential and TDFe in the bottom (hypolimnion) waters of La Plata reservoir.

by external inputs from storm runoff events, and by internal processes brought out by the reductive dissolution of Fe and Mn oxides and/or the mineralization of organic P complexes on the sediment floor. Both mechanisms are particularly evident at this reservoir. Significant increases in total P content in hypolimnion waters were observed under highly reducing conditions (i.e., July to August 2008; September to October 2009). However, major increases were also observed during periods of extreme rainfall (October 2008; April to May 2009). In the latter, increases in total P concentration rose beyond the hypolimnion, thus denoting the mixing effects associated with events of extreme inflows.

### *Nitrogen*

Total nitrogen concentrations support the contention that this is a highly nutrient enriched reservoir and that stringent measures should be taken to restore its ecological integrity. Average total N concentration at the epilimnion was 1.06 mg/L (range 0.41 mg/L to 3.45 mg/L), which is substantially higher than the value established as reference criteria for reservoirs of Puerto Rico (i.e., 0.42 mg TN/L). As observed with P, an increase in average TN concentrations was observed with depth. The average value at the hypolimnion was 1.70 mg/L (range 0.39 mg/L to 3.60 mg/L). These values are high enough to raise concern regarding the ecological sustainability of this reservoir. The sum of ammonium and organic nitrogen moieties [defined by total Kjeldahl

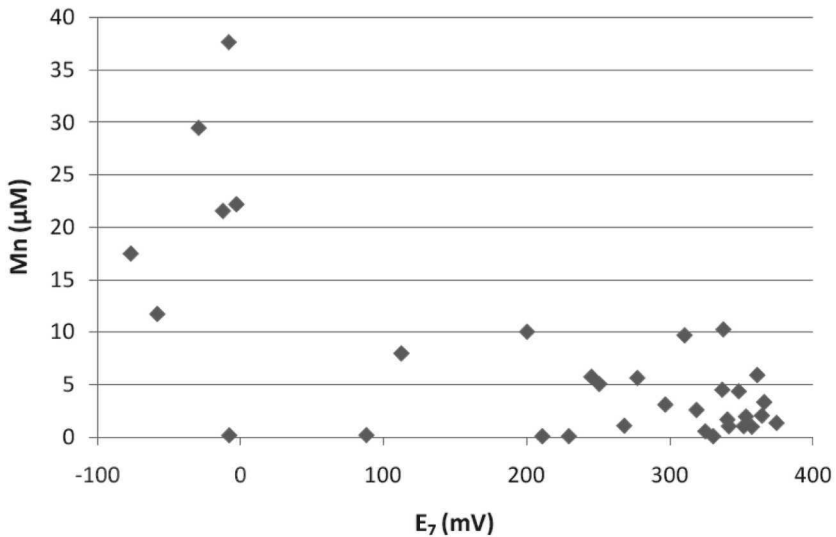


FIGURE 15. Relationship between reduction potential and TDMn in the bottom (hypolimnion) waters of La Plata reservoir.

nitrogen (TKN)] represented 90.8% (range 47 to 100%) of the total N at the epilimnion, whereas at the hypolimnion average contribution was 73.6% (range 36 to 100%) (Figures 8 and 9). The distribution of TKN behaved similarly to that of TP in the sense that major increases were observed during highly reducing conditions and during periods of extreme rainfall (Figure 10). Increases during highly reducing conditions may not be as intuitive as those resulting from intense rainfall events and may point to the release of nitrogen-containing byproducts resulting from the incomplete mineralization of organic compounds.

As stated, nitrate ( $\text{NO}_3\text{-N}$ ) contributed only a small fraction of the total N present at the reservoir. At the epilimnion,  $\text{NO}_3\text{-N}$  contributed an average of 9.6% (range 0 to 52%) of the total N. The relative contribution of  $\text{NO}_3\text{-N}$  was much greater at the hypolimnion with a mean of 28% (range 0 to 64%). Hypolimnetic  $\text{NO}_3\text{-N}$  seems to be associated with contributions of incoming runoff from intense precipitation events. For instance, during 2007-2008, when minimum rainfall was detected (from April to August) nitrate was practically insignificant or completely absent (Figure 11). In contrast, during 2008-2009, the relative presence of nitrate was more significant during a similar period (March to late May) when influenced by a more active rainfall pattern. As conditions turned anoxic in the bottom waters, nitrate became undetectable. This situation is a result of a combination of losses through

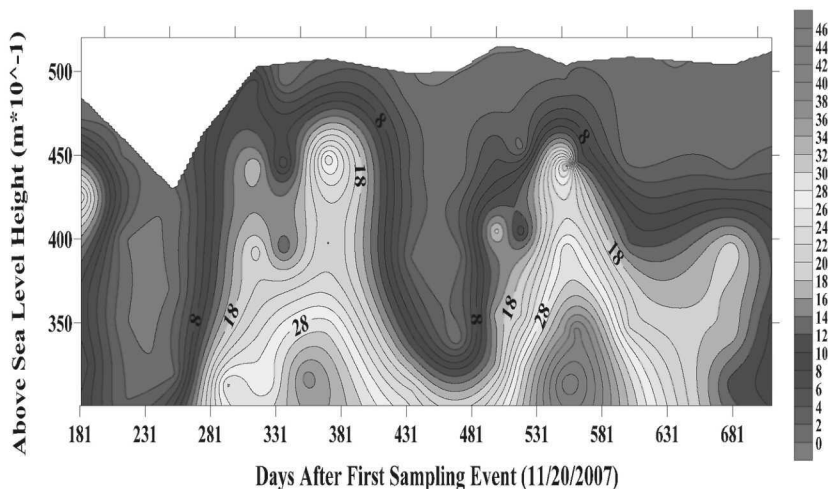


FIGURE 16. Depth-time distribution of total dissolved (TD) Al ( $\mu\text{M}$ ) isopleths at La Plata reservoir.

consumption by biota as well as being due to the denitrification process experienced during highly reducible conditions.

#### *Iron, aluminum and manganese*

The biogeochemical cycling of nutrients and inorganic contaminants in water is largely influenced by the concentration and chemistry of crystalline and amorphous phases of iron and aluminum, as well as by the presence of natural organic molecules. However, the distribution of these metals in lakes and reservoirs is controlled by different mechanisms. The distribution of Fe and Mn is strongly influenced by the redox status of the system (Figures 12, 13). The concentrations of Fe, Al, and Mn at La Plata were significantly higher in the bottom waters than in surface waters. Average epilimnion concentrations for Fe was  $1.12 \mu\text{M}$  (range of  $0.04$  to  $4.12 \mu\text{M}$ ); for Mn it was  $0.20 \mu\text{M}$  (range of  $0.04$  to  $1.41 \mu\text{M}$ ), and for Al was  $1.83 \mu\text{M}$  (range of  $0.44$  to  $10.64 \mu\text{M}$ ). In contrast, the average hypolimnion concentration for Fe was  $14.26 \mu\text{M}$  (range of  $0.04$  to  $61.59 \mu\text{M}$ ); for Mn it was  $8.25 \mu\text{M}$  (range of  $0.04$  to  $37.70 \mu\text{M}$ ), and for Al,  $18.80 \mu\text{M}$  (range of  $0.44$  to  $45.48 \mu\text{M}$ ).

As expected, peaks in Fe and Mn concentrations were negatively correlated to reduction potential showing a sharp increase at  $E_r$  values less than  $0 \text{ mV}$  (Figures 14 and 15). This fluctuation is prompted by the reductive dissolution processes of crystalline and amorphous phases containing these metals under highly reducing conditions. Aluminum, on the other hand, exhibited a pattern that was more related to the

effects of runoff from intense precipitation events. The highest Al concentration peaks were associated with periods of intense rain (9/08 to 10/08 and 5/09), whereas the biggest drops were observed during relatively dry periods where coagulations processes may have promoted settling onto the bottom floor (Figure 16).

## CONCLUSIONS

Incoming flows from moderate to extreme rainfall events significantly influence the general limnological properties of La Plata reservoir in Puerto Rico. The reservoir has a high watershed/surface area ratio. As a result, waters at this reservoir exhibit a short retention time, and complete holomixis during the rainy season is common. In the absence of rain events that bring cool oxygenated water into the system, the reservoir remains thermally stratified during most of the year. In addition, hypolimnion waters remain anoxic, setting off reducing conditions that can be highly detrimental to water quality. Annual mean volume-weighted DO concentrations for the reservoir suggest that its feasibility as a fish reproduction habitat could be compromised at times. Elevated nutrient and chlorophyll *a* concentrations indicate that the reservoir is between the eutrophic-hypereutrophic boundaries. A comprehensive management/restoration plan is needed to prevent further deterioration of the ecological integrity of this reservoir.

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